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Influence of external effects on the electrical properties of high pressure perovskite-like phases $CaCu_3Ti_{4-x}V_xO_{12}$

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Abstract. Samples of high pressure perovskite-like phases $CaCu_3Ti_{4-x}V_xO_{12}$, $x = 0.1$, 0.2, 0.3, 0.4 and 0.5 were synthesized at high-pressure and high-temperature conditions in a toroid-type high-pressure chamber. Their electrical properties were studied by impedance spectroscopy in the frequency range from 1 Hz to 30 MHz at temperatures of 300 to 600 K and at pressures of 10 to 30 GPa.

1. Introduction

In studying materials with a giant dielectric constant, one of the tasks is to find the conditions at which the dielectric constant is substantially independent of the electric field frequency in a wide range of varied external parameters. The aim of the work is to investigate the influence of external effects (temperature, electric field frequency, high pressure) on the electrical properties of the high pressure perovskite-like phases $CaCu_3Ti_{4-x}V_xO_{12}$. These phases were obtained by substitution of titanium with vanadium in $CaCu_3Ti_4O_{12}$ (CCTO) which has a cubic crystal structure and a giant dielectric constant ($\sim 10^4$–10^5) [1].

2. Materials and methods

The ceramic samples $CaCu_3Ti_{4-x}V_xO_{12}$, $x = 0.1$, 0.2, 0.3, 0.4 and 0.5 were synthesized at high-pressure and high-temperature conditions ($P \sim 10$ GPa, $T \sim 1000$°C, $t \sim$ 10–15 min) in a toroid-type high-pressure chamber. The conditions and the equipment of the thermobaric synthesis are described in detail in [2,3]. X-ray diffraction studies (Shimadzu XDR-7000, Cu-K_α-radiation) have shown that all phases crystallize in a cubic symmetry and have a perovskite-like structure. The lattice parameter decreases with successive substitution of titanium for vanadium (figure 1a) due to the difference in the ionic radius of Ti^{4+} and V^{4+} (0.605 Å for Ti^{4+} and 0.58 Å for V^{4+} [4]. The grain size decreases with decrease in titanium content and with addition of vanadium [3].

The electrical properties of the synthesized oxides were studied in a wide range of temperatures and pressures by impedance spectroscopy (Solartron 1260A) in the frequency range of the alternating electric fields from 1 Hz to 30 MHz. The ProboStat cell and the

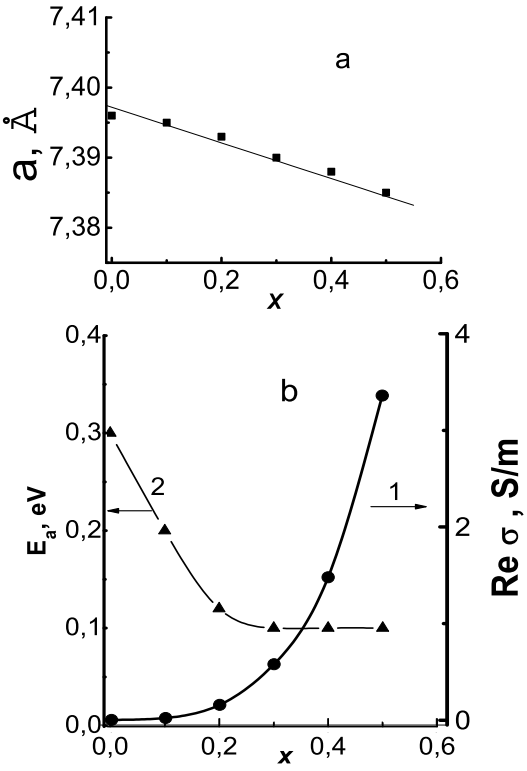

Figure 1. Lattice parameter (a), conductivity (b, curve 1), conductivity activation energy (b, curve 2) of the $CaCu_3Ti_{4-x}V_xO_{12}$ compounds as a function of vanadium content.

ModuLab Materials Test System were used to measure the electrical properties at temperatures from 300 K to 600 K. Analysis of the influence of high pressure on the electrical properties was carried out in the pressure range of 10 to 30 GPa. The pressure values in this range are larger than those used in the synthesis of the materials. The high-pressure measurements of the electrical properties were carried out in a high-pressure chamber (HPC) with anvils made of synthetic carbonado-type diamonds. These anvils have low resistivity and enable examining the electrical properties of the samples placed in the HPC. The pressure estimation and HPC calibration method is described in detail in [5–7].

3. Results and Discussion

With increase in vanadium content in $CaCu_3Ti_{4-x}V_xO_{12}$, the activation energy of conductivity decreases, the electrical conductivity increases and the dielectric constant remains high (figures 1b and 2).

At the same time, the conductivity is independent of the frequency in the range from 100 Hz to 1 MHz, and the dielectric constant remains practically constant in a frequency range from 10^3 to 10^7 Hz (figure 2b). It can be assumed that the mechanism of internal barrier layer capacitance (IBLC) [8] is responsible for the high values of the dielectric constant in the investigated compounds. In the IBLC model, the ceramic is supposed to consist of n-type semiconducting grains and insulating grain boundaries. For the perovskite-like compounds of $ACu_3V_4O_{12}$ (where A is Ca, Gd, Er, Tb), the main features of the electronic states and magnetic interactions are determined primarily by the states of vanadium and copper sublattices and their interactions with the oxygen sublattice [9].

The increase in conductivity with the growth of vanadium content in $CaCu_3Ti_{4-x}V_xO_{12}$ can be related to a decrease in the resistance inside the grains and at the grain boundaries, as suggested by the authors in [10]. The resistivity of grains and grain boundaries decreased monotonically with increase in the V doping percentages. Simultaneously, the grain size

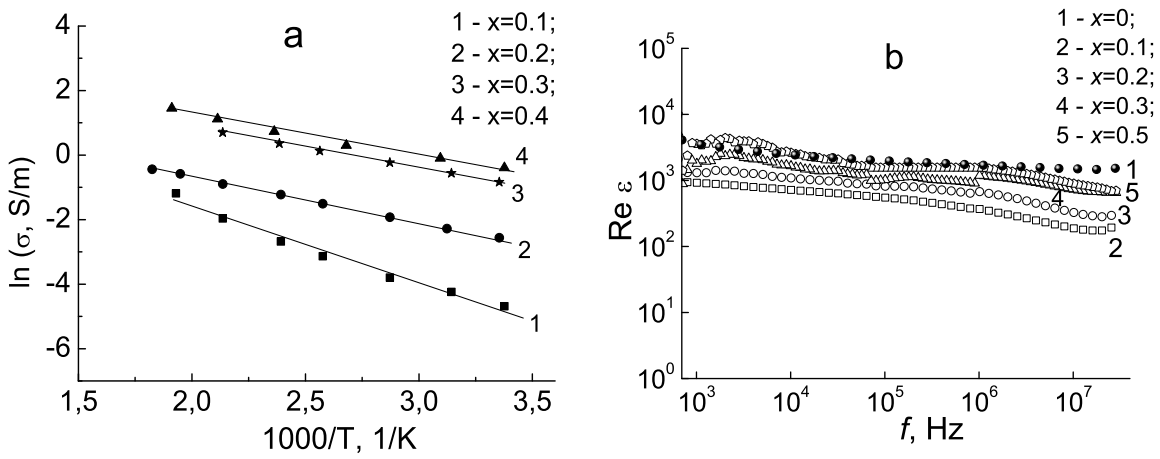

Figure 2. Conductivity as a function of temperature (a) and dielectric constant as a function of frequency (b) for $CaCu_3Ti_{4-x}V_xO_{12}$.

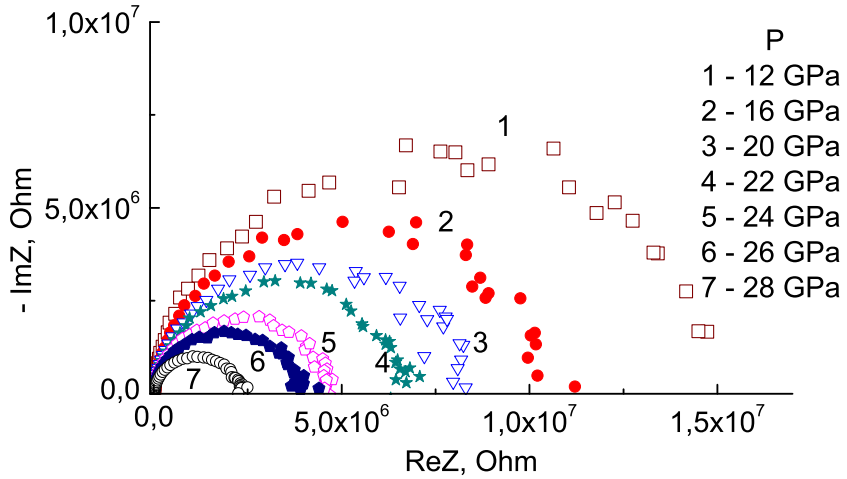

Figure 3. The impedance spectra of $CaCu_3Ti_{4-x}V_xO_{12}$, $x = 0.1$, at indicated fixed pressures P. The measurements were performed at room temperature.

reduction with increase in vanadium content leads to an increase in the total area of grain boundaries, which is one of the major factors in the variation of dielectric properties. The concurrent decrease in resistivity and increase in the grain boundary area sustain the high value of dielectric permittivity with partial substitution of titanium for vanadium in $CaCu_3Ti_{4-x}V_xO_{12}$.

Figure 3 shows the hodographs of impedance of $CaCu_3Ti_{4-x}V_xO_{12}$, $x = 0.1$, at fixed pressures in the range of 10 to 30 GPa. The resistance of the materials was found to decrease with pressure. The logarithm of resistance is a nearly linear function of pressure in the pressure range of interest.

The perovskite-like $ACu_3V_4O_{12}$ compounds (where A is Ca, Gd, Er, Tb) are characterized by similar pressure dependencies of resistivity in the same pressure range [7]. The crystal structure of the compounds is distorted without fundamental restructuring when the pressure increases; the lattice parameter decreases with pressure growth up to 50 GPa [7]. The cubic structure of CCTO is stable up to 57 GPa [11]. A typical property of the $[AC_3](B_4)O_{12}$ compounds with

a perovskite-like structure is that the B–O–B-bond angle φ increases at external pressures and the width of the charge carrier band grows, its value being proportional to $\cos^2\varphi$ [12]. In the compounds under study, the V–O–V and the Ti–O–Ti-bond angle φ may grow with external pressure (at ambient pressure, in the investigated compounds $\varphi \sim 142$–143°), the TiO_6 and VO_6 octahedra are deformed, the width of the conduction band increases, additional electron carriers appear, and electrical resistance decreases. Besides, considering the intergranular effects in ceramics, a decrease in the grain boundary resistivity can be observed at high pressures. This decrease in resistivity may be due to deformation-induced changes in the grain boundary composition. This in turn may decrease the influence of the IBLC effect and, accordingly, the dielectric constant. The preliminary assessment of pressure effects on permittivity based on the capacity of the sample cell indicates high values ($\sim 10^3$) of permittivity in the investigated range of pressures, and the absence of dispersion in the frequency range from 100 Hz to 10^7 Hz. This may indicate that the reasons for high permittivity at high static pressure, as in CCTO [11], may be related both to the features of the crystal structure which remains perovskite-like within the studied pressure range and to the changes in the electrical parameters characterizing the grains and grain boundaries [11]. The features of crystal structure determine polarization, for example, due to the displacement of titanium and vanadium ions during deformation of TiO_6 and VO_6 octahedra with increasing pressure [12].

4. Conclusions

The electrical properties of the ceramic materials $CaCu_3Ti_{4-x}V_xO_{12}$, $x = 0.1$, 0.2, 0.3, 0.4 and 0.5, which were synthesized for the first time by thermobaric method, have been studied by impedance spectroscopy in the broad range of frequencies , temperatures and pressures. Effect of substitution of titanium with vanadium in $CaCu_3Ti_4O_{12}$, which has a giant dielectric constant, on a crystal structure and electrical properties was analyzed. The compounds under study are characterized by a high dielectric permittivity, which remains practically constant in a wide range of electrical field frequencies at normal and high pressures.

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